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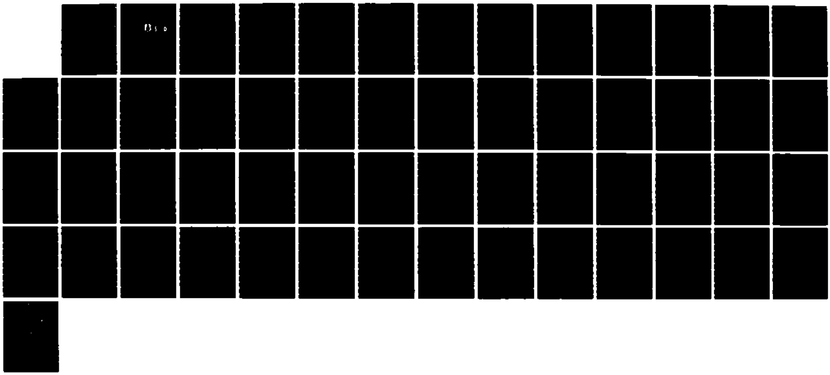

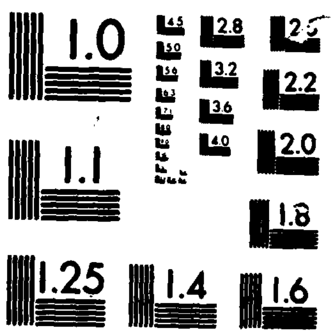

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Research and Development of Laser Glasses in China

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ABSTRACT

Most of the research on laser glasses in China is carried out at Shanghai Institute of Optics and Fine Mechanics, and significant achievements have been made since 1962. A review of the current status of development of laser glasses is presented, including chemical compositions and physical properties, manufacturing technology, measurement and inspection, and some fundamental research.

In the early years of the 60s, laser output was obtained from Nd-doped silicate, borate, phosphate glasses. We made great efforts to develop various Nd-doped silicate glasses for different laser devices and to improve their performance. In recent years development of phosphate and fluophosphate glasses has been emphasized. Several Nd-doped glasses have been produced commercially. The

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spectroscopic, physical, and laser properties of Nd-doped glasses are listed in the appendix of this paper.

We paid more attention to develop a melting process for making laser glass and a protective gas environment melting apparatus was built. Large silicate glass rods of up to 7 cm in diameter and 150 cm long, and phosphate glass discs of up to 30 cm in diameter have been obtained.

Various methods for measuring different kinds of physical properties of laser glasses also have been investigated and the corresponding apparatus have been installed. Emphasis is laid on the inspection of optical quality of large size glass products, and a laser holographic interferometer for optical homogeneity measurement has been developed.

This paper also reports some fundamental research results on laser glasses. By using laser glass spectroscopy, the special properties and structural state of rare earth ions in inorganic glasses were investigated before. The study of spectral and luminescent properties of Nd-doped glasses was emphasized. Further detailed studies of the influence of the glass bases on spectral properties of Nd ion and the energy transfer process of Nd ions in glasses were made. We systematically investigated the intense laser induced damage, thermal blooming, and self-focusing in glass media. Various equipment for measuring non-linear refractive index

of glasses and a new calculation method with accuracy were developed.

Since the invention of the first ruby laser device in the beginning of the 60s, glass research personnel of China began to study the possibility of generating laser beams in glass materials[1]. Snitzer was the first person who reported that laser beams can be produced in Nd-doped silicate glasses[2]. One year later (1963) China also obtained laser output in Nd-doped silicate glasses[3]. In the next year a 100-joule energy output with a total efficiency of 1% was obtained in a glass rod of ø16x500 mm. The generation of the secondary harmonic waves and the spectral result were also reported in the same year[5]. Until 1966 the Nd-glass devices had obtained an energy output of about several thousand joules and a power output of several hundred million watts. This was close to the most advanced level in the world[6]. China is also among the countries who obtained laser beams in borate and phosphate earlier (1965)[4].

All the solid-state high energy and high power laser devices use domestic glasses. Some types of the Nd-glass were already standardized and have entered the stage of pilot plant production. These products are now supplied to about one hundred factories and research institutes. The

economic results are quite good[7].

The following is a summary of the work carried out in recent years.

1. DEVELOPMENT OF ND-DOPED LASER GLASSES

The early Nd-doped laser glasses were all made according to the composition reported by Snitzer, and barium crown glass was used as a base. But such type of glass has poorer chemical stability and poorer resistance against transparancy loss. We changed the glass composition and therefore improved the physical and chemical properties of the glasses. Based on such work we made the first Nd-laser glass, that is the type-1 (N_{01}) glass, in China. This glass met the requirement of the development of China's own Nd-laser devices before 1966. Type-1 glass has shortages such as high processing temperature and large heat expansion coefficient. Therefore a series of crown and borate crown glasses were chosen and their optical-emission and lasing properties after Nd-doping were tested. Finally a Nd-glass with Na_2O-CaO-SiO_2 (a hard crown glass) as the base was chosenand defined as type-3 (N_{03}). Experiments have proved that it has better processing properties, higher chemical stabilities, abd higher mechanical strength than type-1. Now it has become the most mature type of Nd-doped silicate glass in China. The products of this glass, with large sizes

and high quality, can be produced in both Pt and ceramic crucibles.

In order to improve the ability against laser damage (multi-pulse and high energy) and the lifetime of luminescence of optical-emission, and to store more energy in the multi-stage traveling wave amplifier (long duration Xe light pumping), systematic studies of the glass composition adjustment and glass property improvement such as decreasing the heat expansion coefficient, raising the Young's modulus, increasing the mechanical strength, and improving the heat stability were carried out. We have investigated the composition selection of high SiO_2 silicate glasses, the properties of type-4 (N_{04}) Nd-doped glasses (SiO_2>80%) and Nd-doped high SiO_2 glasses (SiO_2>90), and also the composition selection of Nd-doped borate-silicate glasses (R_2O-B_2O_3-SiO_2), that is, the type-6 (N_{06}) glasses. These types of glasses have good heat- and shock-resistance, and also have good resistance against laser-induced damage. Because it was necessary to overcome the processing difficulties such as the requirement for high temperature melting equipment and high temperature crucible materials, and also because it is difficult to obtain good optical properties, the production scale of these glasses was not enlarged. Type-7 (N_{07}) Nd-doped glass is a glass with K_2O-SiO_2 as a base and the concentration of SiO_2 is 80%, the fluorescence

lifetime of this material can reach 800 us, and the device has small super-radiation (fluorescence), and good orientation characteristics of output. But because the excitation emission cross-section area of this glass is smaller, therefore the efficiency of the multi-pulse oscillator using such glass is relatively low. The processing properties of this glass are suitable for the melting process using a ceramic crucible, and large size glass rods with good optical properties have been obtained.

The innomogeneity of optical pumping will lead to heating deformation of Nd-doped glass rods, and therefore the orientation characteristics of output will be degraded by the deformation of the optical routes. According to the experimental results, the decrease of refractive index β and the heat-optical coefficients P, Q, and W will depress this deformation. Based on our investigation of the relation between heat-optical coefficients and glass compositions, we improved the compositions of type-1 and type-2 Nd-doped glasses, prepared and determined the new type-8 (N_{08}) and type-9 (N_{09}) Nd-doped glasses. The heat-optical coefficients p452
were obviously depressed. A prominent problem for applying Nd-doped glasses to high repetition rate devices is heat cracking. In order to improve the resistance against heat cracking, we prepared type-10 (N_{010}) Nd-doped glass. The surface chemical processing with an ion-exchange method can

form prestressing and therefore raise the mechanical strength of this glass. Therefore this glass can meet the requirement of devices with a repetition rate of 1-5 per second.

The spectral, laser, physical, and chemical properties of Nd-doped silicate glasses studied by us in the first 10 years are listed in the appendix. Five of them (N_{03}, N_{07}, N_{08}, N_{09}, N_{010}) have reached a 100-liter production scale. These Nd-doped silicate glasses are included in the main commercial Nd-doped glasses in international markets.

The development of Nd-doped laser glasses in the second 10 years was mainly for meeting the requirement of high power solid state laser devices. The short-pulse high-power laser led to the fact that the damage of laser materials is mainly the non-linear optical effects such as the self-focusing, electrical attraction and expansion, et cetera. The main method to improve the resistance of laser glasses against laser damage is to lower the non-linear refractive indices of the glasses. With the shortened duration of optical pumping, it is required to raise the excitation emission cross-section area of the laser glasses and therefore to improve the laser amplification. Phosphate and fluophosphate glasses can meet the above requirement. Furthermore, they have lower heat-optical coefficients than silicate glasses and therefore can improve the heat deformation

by optical pumping.

Based on the past studies of phosphate and fluophosphate glasses[8], we have intensively investigated the spectral and optical emission properties of these two types of glasses, and the influences on the optical emission and laser properties by the stability of glass formation and chemical stability, and hydroxyl. Since the new processing method was introduced, two new types of Nd-doped phosphate glasses N_{21} and N_{24} have been prepared[9]; N_{21} Nd-doped glass can be processed into glass rods of 70 mm in diameter and discs of 300 mm in diameter. Fluophosphate glasses have lower non-linear refractive indices, lower heat-optical coefficients, and higher quantum efficiencies of optical emission than phosphate glasses. But because this type of glasses is easy to produce, crystal segregation can be easily contaminated by platinum, and it is easy to have selective evaporation of glass composition in the processing[10]. T herefore although the types of Nd-doped fluophosphate glasses were determined, but they have not obtained practical applications yet. The spectral, laser, physical, and chemical properties are listed in table 1.

Table 1. Properties of Nd-doped phosphate and fluophosphate glasses

No.	性质	磷酸盐玻璃		氟磷酸盐玻璃 LFP $2\%Nd_2O_3$
		N_{2112}	N_{2412}	
1.	荧光中心波长(微米)	1.054	1.054	1.053
2.	荧光线半宽度(Å)	265	255	262
3.	荧光寿命(微秒)	350	310	405
4.	受激发射截面($\times 10^{-20}$厘米^2)	3.5	4.0	2.838
5.	荧光分子比($\beta_{1.06}$)	0.52	0.52	0.51
6.	1.06 μm 损耗系数($\times 10^{-2}$厘米$^{-1}$))	1.5	1.5	>5
7.	激光效率* ($\phi 6 \times 150$ 毫米)	1.8	1.5	<1
8.	激光中心波长(Å)	10541.39	—	10532.05
9.	激光谱线宽度(Å)	34	—	21
10.	密度(克/厘米^3)	3.38	2.95	3.52
11.	折射率	1.574	1.543	1.4805
12.	阿贝数	64.5	66.6	83.9
13.	热膨胀系数($\times 10^{-7}$, °C^{-1})	117	156	157
14.	折射率温度系数($\times 10^{-7}$, °C^{-1})	−53	—	−79
15.	热光系数($\times 10^{-7}$, °C^{-1})	7.1	—	−10
16.	应力热光系数($\times 10^{-7}$, °C^{-1})	7	—	7
17.	双折射热光系数(10^{-7}, °C^{-1})	4	—	3
18.	转变温度(°C)	510	370	420
19.	变形温度(°C)	535	410	465
20.	弹性模数(千克/毫米^2)	5550	5370	8259
21.	剪切模数(千克/毫米^2)	2200	2150	3210
22.	泊松比	0.26	0.25	0.28
23.	非线性折射率(10^{-13}esu)	1.3	1.2	0.655

* 两端面反射率 99% 和 50%

1-property; 2-phosphate glass; 3-fluophosphate glass; 4-center wavelength of fluorescence (μm); 5-half width of fluorescence line (Å); 6-life time of fluorescence (μs); 7-cross-section area of excitation emission ($\times 10^{-20}$ cm^2); 8-ratio of fluorescence molecule; 9-1.06 μm loss coefficient

($\times 10^{-3}$ cm^{-1}); 10-laser efficient* (ϕ6x150 mm); 11-center wavelength of laser (Å); 12-spectral line width of laser; 13-density ($gram/cm^3$); 14-refractive index; 15-Abbe number; 16-heat expansion coefficient; 17-temperature coefficient of refractive index; 18-heat-optical coefficient; 19-stress heat-optical coefficient; 20-heat-optical coefficient of double refraction; 21-transfomation temperature; 22-deformation temperature; 23-Young's modulus (kg/mm^2); 24-shear modulus (kg/mm^2); 25-Poisson ratio; 26-non-linear refractive index.

* the reflectivities of the two ends are 99% and 50%, respectively.

2. PROCESSING IMPROVEMENT OF ND-DOPED GLASSES

Compared with optical glasses, Nd-glass require more high purity and optical homogeneity. In order to obtain usable products these requirements must be guaranteed in the process of manufacture. Together with Shanghai Xinhu Glass Plant, we began such processing studies of Nd-doped silicate glasses in 1964. At first we used a Pt crucible for the melting process of Nd-doped glasses in an electric resistance oven. With the increase of device output, the working material was damaged easily. According to our investigation, the main reason for such damage was the Pt particles in glasses. Glasses without Pt particles have several times higher

resistance against laser damage. We prepared Pt-particle free glasses by using two channels as follows.

The first channel is to use an all ceramic crucible for melting process of Nd-doped glasses. The key is to find out the appropriate materials for crucible and stiring blades. It is required that the harmful contents, e.g. Fe, in these materials should be very low (<0.1%), the ability to resist against the erosion of glass should be high, the weight loading capacity should be high enough, et cetera. We have tested crucibles using different materials, and have carried out acid disposal to dissolve Fe in the raw ceramic materials. We also found several new high purity materials; the Fe content of these materials can be below 0.1 % after the fine proposal. Crucibles with a more than 100-liter capacity, using these materials and some melting assistant additions, were already used in the processing of Nd-doped silicate glasses.

But there is a limitation of low impurities of the natural materials and it can not meet the requirement of further lowering the optical loss of Nd-doped glasses. In order to obtain ceramic with higher purity, we have investigated the properties of artificial oxide materials[11-13]. Our artifical oxide materials have been used to make stirring blades in a batch production scale. This has greatly lowered Fe content and improved the

homogeneity of the glasses. Furthermore the result of inner layers using artificial Moley stone is also good.

Using all ceramic systems in the glass melting process will inevitablely introduce line defects, gas bubbles, particles, et cetera, in glass, due to the erosion of the melted glass phase. For many years, we have investigated the source of particles and the process of disappearing of the line defects by stirring the liquid glass[14,15]. Decreasing the temperature of melting process, using low speed stirring, et cetera are effective methods of processing.

The second channel is the Pt depressing testing in a gas environment. That is: the melting process of glass is done in a neutral or reductive gas environment or under a protective layer to avoid the entering of Pt by oxidation. The resistance against laser damage of Pt-free Nd-doped glasses was increased[16]. The high frequency self-heating melting process was also investigated[17]. The glass materials were melted by dielectric loss and during current heating in a 20 MHz electric-magnetic field.

Table 2. A comparison of foreign and domestic Nd-doped glasses

国名	玻璃型号	制造方式	光吸收系数 %厘米$^{-1}$	光学均匀性 Δn(φ毫米)	抗激光破坏强度 焦耳/厘米^2 (30毫微秒)	激光性能: 玻璃棒尺寸 (毫米)	激光性能: 输出端反射率 %	激光性能: 效率 %	激光性能: 斜率 %	资料来源,日期
中国	N_{0330}	铂坩埚	0.1~0.2			φ8×81	40	1.2	4	自己测定,1973
美国	ED-2	除铂工艺	0.3		40(每升含5个破坏点)	φ6×75	70	0.9	—	[51], 1972
日本	LSG-91	除铂工艺	0.1		28	φ6×75	70	1.0	—	[51], 1972
西德	LG-55	陶瓷坩埚	0.5			φ8×79	40	0.7	1.2	自己测定,1973
苏联	КГСС-46	—	0.15			φ8×80	—	0.7~0.8	—	[52], 1969
中国	N_{0330}	铂坩埚	0.2	$<1\times10^{-6}$ (φ 50)		φ14×180	30	2.0	—	自己测定,1968
日本	LCG-11	除铂工艺	0.1~0.2	$\pm5\times10^{-6}$ (φ 50)	28	φ10×160	60	1.1	1.52	产品目录,1971
日本	LSG-91	除铂工艺	0.1		28	φ10×160	60	—	2.0	[51], 1972
西德	LG-630	铂坩埚	0.1~0.2	$\pm2\times10^{-6}$ (φ 30)	—	φ12×170	65	1.5	—	产品目录,1970
苏联	ГЛС-28-2	—	0.1		20	φ10×130	—	1.2	—	展品说明书,1971
苏联	ГЛС-41	—	0.14		—	φ10×130	—	2.0	—	展品说明书,1971
英国	LN-6	陶瓷,池炉	>1		—	φ12×165	30	0.9	—	自己测定,1965
中国	N_{0830}	铂坩埚	0.1			φ16×500	20	5~5.5	—	自己测定,1972
中国	N_{0730}	陶瓷坩埚	0.2	5×10^{-6} (φ 50)		φ16×500	20	4.5	—	自己测定,1972
美国	ED-2	除铂工艺	0.3		40	φ19×510	—	5.5	—	产品目录,1971

1-country; 2-China; 3-USA; 4-Japan; 5-West Germany; 6-USSR; 7-China; 8-Japan; 9-Japan; 10-West Germany; 11-USSR; 12-USSR; 13-England; 14-China; 15-China; 16-USA; 17-Glass type; 18-method of processing; 19-Pt crucible; 20-Pt depressing; 21-Pt depressing; 22-ceramic crucible; 23- Pt crucible; 24-Pt depressing; 25-Pt depressing; 26-Pt crucible; 27-pool type ceramic furnace; 28-Pt crucible; 29-ceramic crucible; 30-Pt depressing; 31-optical absorption coefficient (% cm^{-1}); 32-optical uniformity, Δn(φ mm); 33-

strength to resist laser damage, joule/cm^2, (30 ns): 34-(5 damaged points per liter): 35-laser property: 36-size of glass rod; 37- refractive index at the output end: 38-efficient; 39-slope, % 40-source of information and date: 41-measured by ourselves: 42-product catalog: 43-brochure of exhibited product.

With the above improvement of processing and using Pt crucibles, the following properties can be obtained for Nd-doped silicate glasses: Fe content is as low as 0.01%, optical loss at 1.06 μm is about 0.1% cm^{-1}, and the free oscillating efficiency of a glass rod with size of ϕ16x500 mm can reach 6% (N_{0330}). For Nd-doped glasses melted in a ceramic crucible, Fe content is about 0.02%, optical loss is about 0.2% cm^{-1}, and the efficiency of a glass rod with size of ϕ16x500 mm can reach 4%. Table 2 is a comparison of optical quality and laser properties between foreign and domestic products. The quality of our experimental products is equivalent to that of commercial products of foreign countries. p455

Because phosphate and fluophosphate glasses are very erosive to ceramic materials, therefore these glasses can not be melted in ceramic systems. Furthermore, these glasses are easy to produce crystal segregation and the viscosity in the casting is small. Thus it is difficult to

obtain homogeneous glass products. After many years of investigation, we obtained a method of melting Nd-doped phosphate glasses under a protective layer in a Pt crucible, and obtained the appropriate glass shapes with funnel-type pouring[18,19]. Phosphate glass is easy to absorb water, and the hydroxyls in the glass will extingish the fluorescence of Nd ions; therefore a special water dissolving process is required in the melting process[20, 21]. Currently we can make large-size, high quality Nd-doped phosphate glasses; the efficiency of glass rods with size of ϕ6x100 mm can be about 1.3% (free oscillation), the short-pulse small-signal amplification of such glass rods is 0.16 cm^{-1}, and the amplification in a ϕ200 mm disc-like laser device is 0.048 cm^{-1} (after feedback oscillation is eliminated).

3. CHARACTERIZATION AND QUALITY TESTING OF LASER GLASSES

In the last 10 years, we had built a systematic system of measurement and calculation methods for obtaining spectral and optical emission parameters, e.g. fluorescence energy level, quasi-ground state emission, non-radiative transition probability, quantum efficiency, ratio of fluorescence branches, etc[22]. Table 3 lists $^4F_{3/2}$ and $^4I_{9/2}$ energy levels of Nd^{3+} ions of domestic Nd-doped glasses and the fluorescent transition from $^4F_{3/2}$ to $^4I_{9/2}$. Appendix (4) lists the experimentally determined spectral

parameters of domestic Nd-doped glasses.

Table 3. Some of the fluorescence energy levels(a) and $^4F_{3/2}$ to $^4I_{9/2}$ transition (b) of some Nd-doped silicate glasses

(单位: 厘米$^{-1}$) 1

	玻璃型号 2		N_{0712}	N_{0212}	N_{0812}	N_{0612}
a)	$^4I_{9/2}$	1	0	0	0	0
		2	78	84	79	78
		3	176	180	188	180
		4	262	278	279	280
		5	500	497	498	510
	$^4F_{3/2}$	上 3	11410	11408	11403	11405
		下 4	11580	11577	11578	11572

	玻璃型号 5 / 荧光峰位置 6 / 跃迁 7	N_{0712}		N_{0812}		N_{0812}		N_{0812}	
		λ (埃) 8	ν (厘米$^{-1}$) 9	λ (埃) 8	ν (厘米$^{-1}$) 9	λ (埃) 8	ν (厘米$^{-1}$) 9	λ (埃) 8	ν (厘米$^{-1}$) 9
b)	$^4F_{3/2} \to {}^4I_{9/2}$								
	上→1	8635	11580	8637	11577	8637	11578	8642	11572
	→2	8695	11502	8700	11494	8705	11488	8700	11494
	→3	8770	11403	8775	11397	8780	11390	8780	11390
	→4	8835	11319	8850	11299	8850	11299	8855	11292
	→5	9025	11080	9025	11080	9025	11060	9040	11062
	下→1	8765	11410	8770	11408	8770	11403	8770	11403
	→2	8825	11332	8835	11319	8830	11325	8830	11325
	→3	8900	11236	8910	11222	8915	11215	8910	11223
	→4	8970	11146	8990	11124	8990	11124	8990	11123
	→5	9165	10910	9170	10905	9170	10905	9180	10893

1-(unit: cm^{-1}); 2-type of glass; 3-upper limit; 4-lower limit; 5-type of glass; 6-position of fluorescent peak; 7-type of transition; 8-(Å); 9-(cm^{-1}).

For many years we had paid attention to the heat p454

deformation problem of Nd-doped glass. The relation between heat deformation and some heat-optical coefficients, such as temperature coefficient of refractive index (β), heat-optical coefficient of stress (P), stress coefficient of double refraction (Q), heat-optical coefficient without heat stress were obtained theoretically and confirmed experimentally[23]. Accurate methods of measurement and instruments were built for such measurements[24]. The dynamic process of heat deformation was measured[25]. This has provided a basis for solving the heat deformation problem by further improving the compositions and properties of the glasses.

The damage by intense laser beams is an important problem of research. We have built the measurement methods of the laser-induced damage in Nd-doped glasses by multi-pulse and single-pulse high energy lasers (including in-cavity and out-cavity damages). The damage thresholds of different glasses were determined, and some special damage phanomena were observed. We paid attention to the measurement of non-linear refractive indices. This parameter was measured by self-focus damage threshold[26], self-induction changes of polarization[27], light-induced double refraction[28], and interference method[29].

The homogeneity of large size laser glass is the most important parameter of quality. We have built several

methods for the optical homogeneity testing such as interference method, star-point method, projection method, and image formation method. A systematic evaluation of these methods has been carried out[30]. Later a holographic interference technique was developed and fast sorting was obtained[31]. The line defect and gas bubble were also measured by a holographic method[32]. At the same time, the methods and apparatus for measuring 1.06 μm absorption coefficient and the residual stress in glass rod and disk were improved. In the last 10 years we carried out many measurements and a large quantity of data were gathered. According to the experiments, Fe^{++}-ion content in glass and optical absorption coefficient play the decisive roles for laser efficiency, and their relation was found. The optical homogeneity of glass rods, especially the dense fine lines and physical homogeneity, has serious influence on the orientation characteristics of laser output. The unstability of laser output of Nd-doped glass under multiple optical pumping was investigated. Besides the result that color centers will be produced under ultra-violet irradiation of laser pumping, there is a process of oxidation-reduction reactions which makes the three-valence Fe-ions become two-valence Fe-ions.

In order to evaluate the overall properties of laser glasses, the methods and apparetus for related physical

parameters such as ultra-violet and infra-red refractive indexes[33], stress optical constant, Young's moudulus, et cetera[34], were built. At the same time, calculation methods of glass physical properties, which are closely related to laser glasses, were established.

4. SOME BASIC STUDIES OF LASER GLASSES

In the field of spectral study of laser glasses, the spectral properties and structural status of different rare earth ions in inorganic glasses were investigated in the early years[36]. They were also explained with the theory of distributed potential field.

Table 4. Optical emission properties of Nd^{3+} in inorganic glasses

序	玻璃系统	τ_m (微秒)	$A^{1.06}$ (秒$^{-1}$)		ΣA_r (秒$^{-1}$)		ΣA_{nr} (秒$^{-1}$)		η		$\sigma_p^{1.06}$, $\times 10^{-20}$ (厘米^2)	
			测量	计算	测量	计算	测量	计算	测量	计算	测量	计算
1	硼酸盐	90	1220	1284	2416	2666	8695	8445	0.22	0.24	2.35	2.46
2	硅酸盐	510	856	907	1793	1849	168	112	0.91	0.94	1.90	2.01
3	锗酸盐	370	1152	1118	2425	2256	278	346	0.90	0.87	2.51	2.43
4	磷酸盐	220	2914	2574	5950	5272	~0	~0	~1.0	~1.0	5.05	4.46
5	碲酸盐	280	1405	1238	2831	2360	740	1210	0.79	0.67	4.46	3.92
6	铝酸盐	200	1728	2164	4028	4645	972	355	0.81	0.93	2.9	3.60
7	铝硅酸盐	200	1170	1499	2704	3123	2296	1877	0.54	0.62	1.9	2.4
8	镓锗酸盐	350	1147	1258	2208	2579	559	278	0.80	0.90	1.8	2.0
9	氟磷酸盐	475	1007	859	1890	1811	215	294	0.90	0.86	2.5	2.2
10	氟铍酸盐	600	700	697	1200	1285	380	382	0.77	0.77	2.15	2.15

注: ΣA_{nr} 为无辐射跃迁几率; ΣA_r 为辐射跃迁几率; η 为量子效率; σ_p 为受激发射截面。

1-No.; 2-type of glass; 3-μs; 4-measured result; 5-calculated result; 6-total; 7-cm^2; 8-borate; 9-silicate; 10-germanate; 11-tellurate; 12-phosphate; 13-aluminate; 14-aluminate-silicate; 15-gallate-silicate; 16-fluophosphate; 17-fluoberyllate; 18-note: ΣA_{nr} is probability of non-radiative transition, ΣA_r is probability of radiative transition; η is quantum efficiency, σ_p is cross-section area of excited emission.

Later we carried out an intensive investigation on the spectral and optical emission properties, especially on the influence of micro and sub-micro structures to the spectral and optical emission properties[37]. We first investigated silicate based glasses, then the other inorganic glasses such as borate, phosphate, germanate, tellurate, fluophosphate, and fluoride. The influence of glass bases to excitation ions is mainly reflected in their interactions. The static electrical interaction between distributed potential field and Nd^{3+} causes a splitting of spectral line (or energy levels). According to the splitting values Δs of ground state $^4I_{9/2}$ and the final state $^4I_{11/2}$ of Nd^{3+} in the Nd-doped crystal and glass, we have summarized that the splitting value Δ, in a base with ionic bonds as the major bonding, is correlated to the interaction force between the field distributing bodies (anions), and this relation can be p455

expressed with a simple formula $F=3z/a^2$, here x is the valence of anions, a is the sum of the two radii, and Δ increases with the increase of F. If some anion clusters appear in the base material, such as SiO_4^{-4}, PO_4^{-3}, etc, the influence of the field distributing body to Nd^{3+} will decrease and Δ will also decrease. The increased interaction between the central cation and oxygen anion $O^{=}$ in oxygen cluster $[RO_x]$ will weaken the influence of oxygen ions on Nd^{3+}, that is, the Δ will decrease with the increase of F', $F'=2z'/a^2$, here z' is the valence of the central action (see figure 1.) Different from ionic crystals, the strong *influence of base glass to excitation ion is reflected in* their polarization, that is: the factor of covalent bonds. Such influence was first observed in the moving of spectral lines (see figure 2). We use the electrical negativity difference between anion and cation, Δx, to explain this effect[38]. Polarization has more obvious effects on the transition probability of the excitation ions. We further investigated the energy transfer process of Nd^{3+} ions in inorganic glasses[39]. We also investigated the probabilities of radiative and non-radiative transitions, the excited emission cross-section areas, and quantum efficiencies of 10 different Nd-doped glasses as listed in table 4[40]. It was found that the influence of base glass on non-radiative transition was much larger than on

radiative tansition. In inorganic glasses, the non-radiative transition caused by the interactions between Nd^{3+} ions and other rare earth ions or transition element ions are processes of resonant transfer or phonon-assistant relaxation. The energy transition due to the interaction between Nd^{3+} and anions (e.g. OH and $O^{=}$) was treated by the multi-phonon model which was widely used in the world[41,42]. But due to the complicated phonon modes of inorganic glasses, no satisfactory results were obtained. This is possibly an energy transfer process of inner molecules and further investigation is being done.

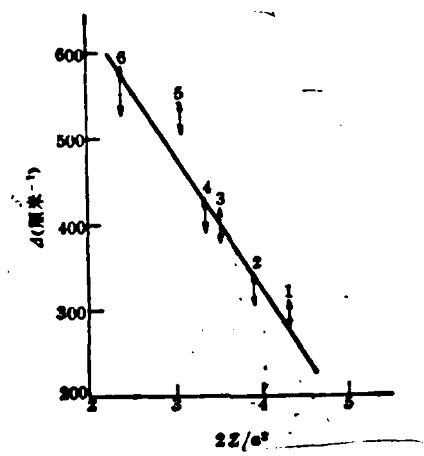

Fig. 1. Relation between splitting value of the spectral term $^4I_{9/2}$ and the Coulomb interaction of oxygen ion groups 1-phosphate; 2-tungstate and molybdenate; 3-arsenate; 4-vanadate; 5-silicate; 6-borate; 7-niobate-tantalate; 8-cm.

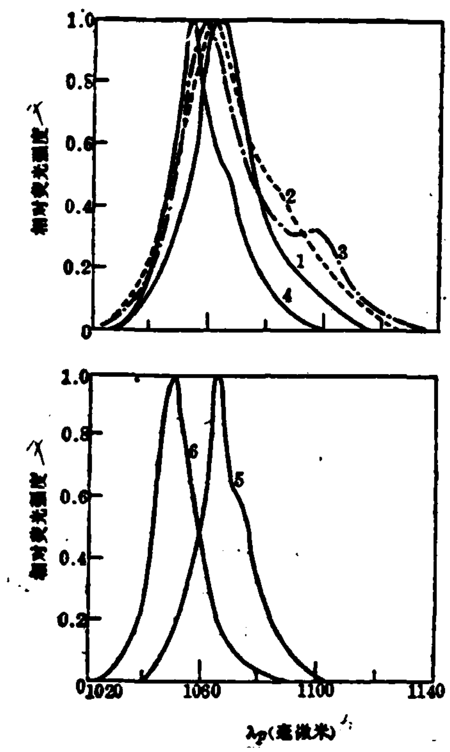

Fig. 2. Spectra of different Nd-doped glasses.
1-tellurate; 2-borate; 3-Silicate; 4-phosphate; 5-chloride; 6-fluorate; 7-relative intensity of fluorescence; 8-nano µm.

In order to develop new types of laser glass, mainly invisible and infra-red laser glasses and tunable laser p456 glasses, we have carried out further studies of spectral and

optical emission properties of glasses doped by ions of transition elements, actinum family elements, and other rare earth elements. Until now we have investigated fluorescence and time resolved spectra, excited by parallel magnetic resonance and laser excitation, of Cr^{3+}, Mo^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, UO_2^{2+}, etc[43-45, 53]. We also have investigated the energy transfer process from Ce^{3+} to Tb^{3+}, Tm^{3+}, Er^{3+}, and from Nd^{3+} to Yb^{3+}[46].

We have also investigated systematically the interactions between intense laser beam and the glass mediums. The work done in the early stage was mainly in the following three aspects: (1) heat deformation due to free oscillations, this is defined as optical beam blooming; (2) self-focus due to short-pulse laser beam; (3) glass damage caused by laser beam. Based on the above experiments, we think the interaction between laser beam and glass medium is caused by the following effects: heat effect, electrical expansion and attraction, and non-linear polarization. The corresponding non-linear refractive indices are $n_2(T)$, $n_2(S)$, $n_2(E)$[47]. We developed a new method to calculate the accurate values of these three refractive indices according to the known physical properties[48,49]. For a comparison, table 5 lists the calculated results and measurement values of non-linear refractive index $n_2(E)$; the methods of measurement are self-damage threshold(SF), self-induction

polarization (SIPC), and light-induced double refraction (LIB). Which of these three non-linear optical effects is the major effect depends on pulse time of the laser beam. Table 6 lists these three non-linear refractive indices, under three different situations of laser pulse, of N_{03} laser glass. We can know that for continuous and milli-second pulse lasers the main interaction between laser and glass is heat effect, but for nano-second and sub-nano-second pulse lasers the main interaction between laser and glass is non-linear polarization. Therefore we established the relation between the non-linear optical effects in glass and the physical properties. Figure 3 shows the relation between $n_2(E)$ and the laser damage threshold of some optical and laser glasses, caused by nano-second pulse laser beams. Figure 4 shows the relation between $n_2(T)$ and the heat blooming in glasses caused by nano second laser pulses ($\Delta\theta/E_A$, $\Delta\theta$ is the dispersive angle of laser output, E_A is the absorbed energy per unit volume of glass).

Table 5. Experimenatal and calculated values of non-linear refractive indexes of some optical and laser glasses

玻璃		测定值 (10^{-13}, esu)			计算值 $n_2(E)$ (10^{-13}, esu)
		SF	SIPC	LIB	
光学玻璃	ZF-7	6.4	7.5	8.3	9.0
	BaF-2	4.1	3.0	3.0	3.6
	QK-3	1.3	—	—	1.2
激光玻璃	N_{0312}	1.9	2.0	2.0	1.7
	N_{0812}	1.6	1.8	2.0	1.9
	N_{1012}	1.6	1.8	2.0	1.7
	N_{2112}	1.3	2.0	1.2	1.5

1-type of glass; 2-optical glass; 3-laser glass; 4-measured result; 5-calculated result.

Table 6. Non-linear refractive indices of N_{03} laser glass under different laser pulse widths

非线性效应	响应时间 (秒)	非线性折射率 n_2 (厘米²/瓦)		
		毫秒脉冲	微秒脉冲	毫微秒脉冲
热效应	$10^{-6}\sim10^{-7}$	6×10^{-12}	6×10^{-15}	—
电致伸缩效应	$10^{-7}\sim10^{-8}$	1.06×10^{-16}	1.06×10^{-16}	1.06×10^{-16}
非线性极化效应	$10^{-15}\sim10^{-16}$	0.92×10^{-15}	0.92×10^{-15}	0.92×10^{-15}

1-non-linear effect; 2-heat effect; 3-electric expansion and attraction effect; 4-non-linear polarization effect; 5-response time; 6-non-linear refractive index; 7-cm^2/watt; 8-milli-second pulse; 9-micro-second pulse; 10-nano-second pulse.

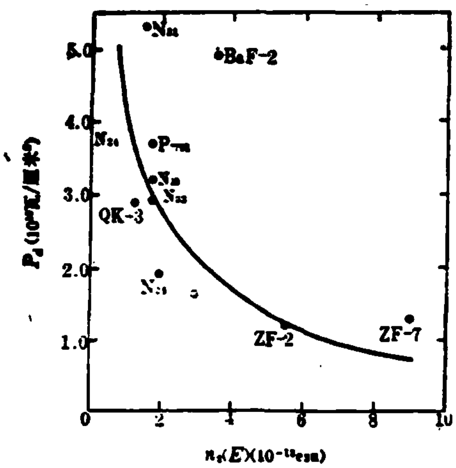

Fig. 3. Relation between n_2(E) and laser damage threshold
1-watt/cm^2.

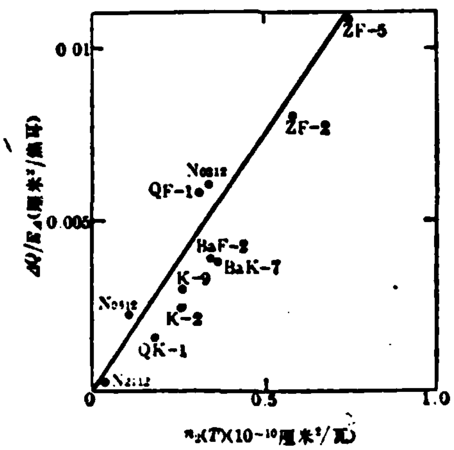

Fig. 4. Relation between n_2(T) and heat blooming effect of glasses
1-cm^2/joule; 2-cm^2/watt.

With the development towards shorter wavelength of laser emission beams, laser damage and non-linear refractive indices at different wavelength become more important. We shall continue to work on these problems both experimentally and theoretically[50].

Part of the data of this paper is referenced from "the Research report of Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, No. 2, 1974; and Laser Materials and Devices, No.8, 1980.

Appendix

Properties of domestic Nd-doped silicate glasses

1. Physical and processing properties

牌号	物理性质						工艺性质		
	密度 (克/厘米³)	显微硬度 (公斤/毫米²)	机械强度 (公斤/毫米²)	弹性模量 (10^3公斤/厘米²)	膨胀系数 10^{-7} °C^{-1} 15°C~200°C	膨胀系数 10^{-7} °C^{-1} 15°C~T_g	转变温度 T_g(°C)	软化温度 T_f(°C)	粘度100泊时的温度 (°C)
N[illegible]	2.90	560	9.7	679	90	104	500	590	1400
N[illegible]	2.87	560	9.0	720	83	91	560	630	1380
N[illegible]	2.51	606	11.8	759	80	88	590	660	1430
N[illegible]	2.49	615	9.4	727	52	57	590	670	1660
N[illegible]	2.52	623	10.4	810	87	95	555	610	1270
N[illegible]	2.52	557	9.1	647	89	96	495	560	1470
N[illegible]	2.80	551	9.1	647	107	120	545	600	1440
N[illegible]	2.50	533	10.2	687	87	93	620	680	1450
N[illegible]	2.52	585	8.9	750	89	100	525	585	1420

1-type; 2-physics properties; 3-processing property; 4-density; 5-microscopic hardness; 6-mechanical strength; 7-Young's modulus; 8-expansion coefficient; 9-transformation temperature; 10-soften temperature; 11-temperature at viscosity of 100 poise.

2. Refractive indices and dispersion

型 号	埚 号	折射率							
		n_C	n_D	n_e	n_F	n_F-n_C	ν	$n_{1.06}$ 测定	$n_{1.06}$ 计算
N[illegible]	C72-13	1.53965	1.5424		1.54898	0.00933	58.14	1.5316	1.5315
N[illegible]	E70-05	1.53860	1.5413		1.54768	0.00908	59.5		1.5307
N[illegible]	D904	1.51969	1.5224	1.52446	1.52843	0.00874	59.8	1.5122	1.5122
N[illegible]	C7215	1.49969	1.5021		1.50774	0.00805	62.5	1.4923	1.4927
N[illegible]	E70-13	1.51725	1.5197		1.52549	0.00824	63.1	1.5136	1.5100
N[illegible]	D865	1.50290	1.5054	1.50746	1.51134	0.00844	59.9	1.4953	1.4955
N[illegible]	C7133	1.53271	1.5354		1.54191	0.00920	58.2	1.5248	1.5246
N[illegible]	D926	1.51502	1.5176	1.51972	1.52363	0.00861	60.1	1.5076	1.5075
N[illegible]	B71-07	1.51455	1.5171		1.52335	0.00880	58.8	1.5067	1.5066

1-type; 2-No. of crucible; 3-refractive index; 4-measured value; 5-calculated value.

3. Heat-optical properties

型 号	$\beta(10^{-6}, °C^{-1})$	$W(10^{-6}, °C^{-1})$	$P(10^{-6}, °C^{-1})$	$Q(10^{-6}, °C^{-1})$	应力光学常数 (10^{-6}, 厘米^2/公斤)	
					$-C_1$	$-C_2$
N_{01}	−0.36	4	5.0	0.8	0.15	0.38
N_{02}	0.13	4.6	4.9	1.0	0.12	0.42
N_{03}	1.64	5.8	4.0	0.9	0.11	0.36
N_{04}	4.17	6.8	2.7	0.8	0.08	0.37
N_{06}	−0.20	4.3	4.9	1.0	0.10	0.35
N_{07}	0.20	4.5	4.0	1.1	0.11	0.40
N_{08}	−3.20	2.5	5.5	1.0	0.09	0.38
N_{09}	0.12	4.6	4.2	1.0	0.11	0.37
N_{10}	0.90	5.4	4.6	1.0	0.09	0.35

1-type; 2-stress optical constant; 3-cm^2/kg.

4. Spectral parameters

玻璃型号	主要成份	荧光分支比			$A_{(0.88)}$ (秒$^{-1}$)	$A_{(1.06)}$ (秒$^{-1}$)	$A_{(1.35)}$ (秒$^{-1}$)	$\sum A_{rt}$ (秒$^{-1}$)	τ (微秒)	$\sum A_{nj}$ (秒$^{-1}$)	η (%)	$\Delta\lambda^{e}_{(0.88)}$ (埃)	$\Delta\lambda^{F}_{(1.06)}$ (埃)	$\sigma^{e}_{p(0.88)}$ ($\times 10^{-20}$ 厘米^2)	$\sigma^{F}_{p(1.06)}$ ($\times 10^{-20}$ 厘米^2)
		$\beta_{0.88}$	$\beta_{1.06}$	$\beta_{1.35}$											
N_{0112}	SiO_2-K_2O-BaO	40	50	10	410	513	100	1024	600	640	61	220	380	0.26	1.00
N_{0212}	SiO_2-B_2O_3-K_2O-BaO	41	49	10	427	513	100	1038	620	575	64	230	360	0.26	1.04
N_{0312}	SiO_2-Na_2O-K_2O-CaO	38	53	9	520	719	124	1364	590	331	81	230	395	0.32	1.35
N_{0412}	SiO_2-K_2O-CaO	41	45	14	477	524	163	1159	680	312	79	260	370	0.26	1.05
N_{0612}	SiO_2-B_2O_3-NaO-K_2O	45	47	9	405	424	81	904	680	367	62	260	360	0.22	0.87
N_{0712}	SiO_2-NaO-K_2O	46	46	8	330	330	57	725	890	399	65	250	335	0.19	0.73
N_{0812}	SiO_2-BaO-K_2O	37	52	11	426	600	127	1156	760	160	88	270	400	0.23	1.11
N_{0912}	SiO_2-CaO-K_2O	42	48	9	405	460	87	959	750	374	72	250	360	0.23	0.95
N_{1024}	SiO_2-CaO-N_2O	35	54	12	470	725	161	1355	510	606	69	240	370	0.29	1.45

1-type of glass; 2-main composition; 3-ratio of fluorescence branches; 4-sec^{-1}; 5-micro-second; 6-A; 7-cm^2.

5. Laser properties

型号	1.06微米光吸收系数 (%厘米$^{-1}$)	ϕ16×500毫米棒的激光效率* (%)	激光中心波长 (Å)	激光谱线宽度 (Å)
N_{0112}	0.2	2.4	—	—
N_{0212}	0.1	3.0	—	—
N_{0312}	0.1	4.0	10624.53	94
N_{0412}	0.16	3.8	10613.21	90
N_{0612}	0.29	2.2	10604.27	124
N_{0712}	0.12	3.5	10584.14	62
N_{0812}	0.27	2.7	10597.89	112
N_{0212}	0.10	3.8	10608.61	109
N_{1024}	0.22	3.5	10611.39	91

* 端面反射率100%与50%，发光时间3毫秒，输入能量1×10^{4}焦耳。

1-type; 2-1.06 μm optical absorption coefficient (% cm^{-1}); 3-laser efficiency of o16x500 mm rod*; 4-central laser wavelength; width of laser spectra line. 6-* reflectivities of end surfaces are 100 % and 50 %, emission time is 3 milli-second; input energy is 1x10^4 joule.

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The Research Progress on Laser Crystals in China

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ABSTRACT

A general review is made on the past and future of the research progress on laser crystals in China. Some proposals are offered in order to open up a new prospect for the development of laser crystals.

In memory of the 10th anniversary of the publishing of "Chinese Journal of Lasers" we are glad to review the course of development of the science and technology of lasers since 1961 in China. The Chinese made laser crystals had played an important role for the birth of the first chinese laser device and the later developments. The Changchun Institute of Optics and Fine Mechanics and Suzhou precious Stone Plant, together with other institutions, had laid the foundation of China's laser crystals. Now we have laser crystal research programs of certain scale, and such research work is being done in more than 30 institutions; more than 1000 scientists

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and technicians are involved; and more than 20 laser crystals are under study. Nd-doped YAG and Cr-doped Al_2O_3 crystals have been produced and obtained wide apllications. Some new promising crystals are under intensive study and are ready for application. Basic research is also being carried out.

I. RARE EARTH ION LASER CRYSTALS

(1). Nd:YAG

China began to grew YAG crystals in 1965. At first, a laser was obtained with crystals prepared by salt-melting method. Nd:YAG crystals with size of up to 0.50mm in diameter were prepared by salt-melting method. Nd:YAG crystals were produced by upward pulling method in 1967. The upward pulling method with electrical resistance heating using a graphite or tungsten heater was popularized in several dozen of institutions. Southwest Institute of Applied Physics developed a set of processing technology to control the growth of plan boundary for obtaining particle-free and dislocation-free Nd:YAG crystals. Recently Sichun Huaguang Plant of Instruments produced crystals with good homogeneity (the interference pattern line density can be as low as 0.25/25 mm). The graphite-resistance method has problems of producing a large number of scattering centers

in crystals. Shanghai Jiaotong University had applied the controlled gas environment to depress scattering centers in some degree. By the upward-pulling method using a Er crucible and electric-magnetic induction heating, scattering partical-free crystals with a diameter of ϕ25-30 mm and a convex boundary surface can be produced. Recently North China Research Institute of Electro-Optics has produced crystals with diameters of ϕ35-40 mm, and the crystal rod of ϕ9x75 which can be used for laser amplification has an interference line density of 0.3/25 mm. Jiling Laser Materials Plant is the bigest plant specialized in YAG crystals; and Chengdu Liming Mechanical Plant is active in developing YAG crystal production. p401

The property of crystals, produced either by electrical resistance method, or induction method, can be improved after high temperature annealing. This shows that oxygen vacancy defects or OH^-s were introduced when the oxide crystal was grown in a reductive or inert gas environment. Some crystals had serious crystal defects or serious harmful impurity contamination; they caused color change after annealing and the optical absorption and scattering loss were increased obviously. The annealing process can uncover the problems existing in crystals and therefore can prevent the poor-quality crystals from being used.

National scale characterization of Nd-YAG laser crystal

rods was organized for two times. It played a good role in stimulating technical communication, improving quality of crystals, and making standard characterization methods. The technology of crystal selection, optical processing, and anti-reflective films at the end surfaces have been improved. The ultrasonic rod picking technique of raw crystal and multi-rod processing technique of crystal end surfaces will be used soon.

Through the investigation of Nd-Cr double doping of YAG crystals made at North China Research Institute of Electro-Optics, it was found that Cr^{3+} has some sensitization effect in Nd:YAG crystals, can improve crystal deformation, increase the lifetime of fluorescence of Nd^{3+} and improve the resistance against ultra-violate beam irradiation. Nd:Cr:YAG crystal has been applied to the hole drilling of ruby bearing, distance measurement, and medical applications.

(2) $YAlO_3$

This crystal was produced in 1971 and produced a laser beam in 1972. Because this crystal is more sensitive to the quality of raw materials and impurities, and the gas environment of growth and annealing also have obvious effects, the graphite-molybdenum growth system was discarded gradually. Basic studies, of the heat-optical properties, transition cross-section areas, and applications of $YAlO_3$ crystal, were made at Shanghai Research Institute

of Optics and Fine Mechanics. Since the 70s, most institutions switched their investigation to YAG, and only Fujian Research Institute of Material Structures insisted in the investigation of $YAlO_3$. They have done good work in crystal growth, material purification, and heat effect of $YAlO_3$. b-axis $Nd:Cr:YAlO_3$ has reached a 162 watt continuous output at 1.079 μm and a 20 watt continuous output at 1.34 μm. This is in the leading position in the world. They also produced $Er:YAlO_3$ crystals and made studies of the spectral properties.

(3) $LiYF_4$ (YLF)

For meeting the requirements of some new wavelengths, North China Research Institute of Electro-Optics began to produce YLF crystals in 1977. A set of technology of inert gas environment and upward pulling method using graphite apparatus was developed. The problems which are keys for crystal quality such as: oxygen content in materials, transparancy loss, twin crystals, and scattering particles were solved. Nd:YLF (1.047 μm, 1.053 μm, and 1.32 μm), Er:YLF (0.85 μm) and αβ-YLF (2.06 μm) have produced laser output at room temperature. Nd:YLF pulse laser output has reached 838 milli-joule and the efficiency has reached 1.51% (maximum is 1.73%). The mode-lock laser operation has been obtained in oscillators using Nd:YLF crystals.

(4) Self exciting laser crystals

Shangtong University and other institutions have produced NdP_5O_{14}, (Nd, La)P_5O_{14}, and $NdAl_3(BO_3)_4$ crystals which are transparent. The size of these crystals has reached 4 cm and this is at the leading position in the world. NdP_5O_{14} using Xe lamp for optical pumping produced laser output in 1979 and was applied to laser distance measurement. (Nd,La)P_5O_{14} and $NdAl_3(BO_3)_4$ generated laser output and they have better properties than NdP_5O_{14}. Fujian Research Institute of Material Structures produced small crystals of Nd:$GdAl_3(BO_3)_4$ and the pulse laser operation was obtained in 1980.

Shanghai Institute of Optics and Fine Mechanics and Shanghai Institute of Ceramics have produced $NdLiP_4O_{12}$ crystals and obtained laser output. In order to decrease harmonic oscillation loss of this crystal, Shanghai Institute of Ceramics has produced $Nd_{0.5}La_{0.5}LiP_4O_{12}$ crystals. A decrease of laser threshold in this crystal is anticipated.

Peking Institute of Artificial Crystals has produced NdP_5O_{14} glass laser rods and obtained laser operation with a rate of 15-20 sec^{-1}. Applications in the field of medicine are anticipated for this crystal.

2. TRANSITION METAL ION LASER CRYSTALS

(1) Ruby crystal (Cr:Al_2O_3)

After the booming period in the 1960's of fire-melting processing

investigation, there was a blank period for the research on ruby crystals. Using upward pulling method, Anhei Institute of Optics and Fine Mechanics and Suzhou plant of Crystals obtained crystals with better homogeneity, in the middle of the 70s. Cooperating with Shanghai Institute of Ceramics and Shanghai Institute of Optics and Fine Mechanics, Jiaozao Institute of Lasers improved the fire-melting method and improved the crystal quality; the laser efficiency reached 1.7% and this institute became the main supplier of this crystal. Recently Annui Institute of Optics and Fine Mechanics and Jiozao Institute of lasers are solving the major problems of upward pulling method and investigating ruby crystals for holography.

(2) Chrysobery ($Cr:BeAl_2O_4$)

This is an end-phonon tunable laser crystal which is being paid attention abroad. Because of the extremely toxic nature of BeO, it is only investigated at Shanghai Institute of Optics and Fine Mechanics, and at Annui Institute of Optics and Fine Mechanics. Shanghai Institute of Optics and Fine Mechanics began to investigate crystal growth in 1981, and obtain laser output in the same year. Recently tunable laser output was observed in this crystal. Anhui Institute of Optics and Fine Mechanics has produced crystals with different crystal axes.

(3) $Ni:MgF_2$

Shanghai Institute of Optics and Fine Mechanics, Shanghai Jiaotong University, and Peking Institute of Glasses have produced $Ni:MgF_2$ single crystals of ϕ24-30x30 mm, by using a sealed graphite crucible and a temperature gradient method. Seed crystals with different crystal orientations have been used for crystal growth. Crystal cracking and stress characteristics have been investigated. Spectral property, dislocation, and line defects were measured. Shanghai Institute of Optics and Fine Mechanics has produced $Co:MgF_2$. Shanghai Jiaotong University has produced Ni:MgO crystals and produced low temperature laser devices.

3. COLOR CENTER LASER CRYSTALS

In the begining of the 80s China had about 10 institutions doing investigations of color center laser crystals. Undoped and doped LiF, KCl, and NaF color center crystals have been produced. Preliminary studies of the formation, types, type transfer treatment, and stability of color centers, etc. have been carried out. LiF with Nd:YAG double frequency pumping produced tunable color center pulse output at room temperature in 1981. Because this program is related to material, device, and applications, and it also can stimulate the related basic research, therefore Huaqiao University and other institutions are doing cooperative

investigations.

4. INVESTIGATION OF NEW LASER MATERIALS

Since the 70s, in order to meet the need of multi-type development of solid laser devices, some institutions of China began to investigate new laser materials. North China Research Institute of Electro-Optics has produced new laser materials such as: $Nd:Ca_5(PO_4)_3F$, $Nd:CaY_4(SiO_4)_3O$, $Nd:YVO_4$, and different rare earth element doped new laser materials such as $Gd_2(MoO_4)_3$ and $Ca_5Y_{13}F_{49}$. Recently new multi-function crystals with self Q- adjustment and mode self-lock functions are under investigation. Cooperating with Peking Institute of Glasses, new end-phonon laser crystals are also under investigation. Fujian Institute of Material Structures is investigating the relation between structures and properties, and has suggested to find new end-phonon transition laser crystals through the channel of combining the crystal dynamics and lattice field theory. Based on the structural characteristics, a new crystal $Cr:YAl_3(BO_3)_4$ was produced. A R-line located in a 684 nanometer was observed in the spectral studies, and there is a very strong phonon band in the 690-750 nanometer region. Shanghai Institute of Optics and Fine Mechanics has carried out spectral studies of some rare earth and transition metal ion doped oxide and fluolides. Anhui Institute of Optics and Fine Mechanics is

investigating new type end-phonon laser crystals by salt-melting methods. Changcheng Institute of Applied Chemistry has produced a series of small size self excited laser crystals with new wavelengths such as: $KNdP_4O_{12}$, $Mn:CeP_5O_{14}$, $Tb_xDy_{1-x}P_5O_{14}$, ect. Shanghai Institute of Ceramics has produced same composition melted $K_5Bi_{0.9}Er_{0.1}(MoO_4)_4$ single crystals and carried out structural and spectral studies. Peking Institute of Physics has investigated the crystal growth and properties of Eu:GGG, Tb:GGG, etc. Several universities are also carrying out basic research for exploiting new materials.

5. FACILITY BUILDING OF LASER CRYSTAL RESEARCH

Before 1960 the crystal growth and property characterization in China were very weak; most of the fields were blank. The invention of lasers greatly had pushed the facility building of crystal research. In order to meet the requirement of the growth of high melting temperature oxides, several upward pulling single crystal furnaces with high precision mechanical movement and high stability were designed and manufactured at Shanghai Institute of Optics and Fine Mechanics, Shanxi Institute of Mechanical Engineering, North China Research Institute of Electro-Optics, Tianjin University, Chongqing University, and other

institutions. Some institutions have developed programmable semi-automatic temperature control systems, automatic mechanic weighting systems, automatic electronic weighting systems, and programmable automatic movement correction systems. The reliability of most of these control systems needs further improvement, the electronic weighting systems are not stable. Experiments of automatic systems using microcomputers are being done now. p465

Kunming Institute of Precious Metals developed in the 1960's technology for product processing of Er, and has supplied different Er products for the growth of high melting oxides by induction methods.

North China Research Institute of Electro-Optics in the 1970's designed and manufactured SCR (silicon controlled rectifier) medium frequency converter power source which has high long-term stability, and it was applied to the crystal growth by the upward pulling method. Because the frequency selection matches the skin effect of Er crucibles, the medium frequency has no influence to control circuits, and it also has small effect on human bodies. This power source was popularized in China. This institute also has developed a laser spectroscope for quantitative measurement of the distribution of excitation ions.

Shanghai Institute of Optics and Fine Mechanics has succeeded in an improved directional temperature gradient

method of crystal growth. Except the application in the growth of white jade single crystals, it is used to produce large diameter Nd:YAG crystals at Shanghai Institute of Optics and Fine mechanics and Changcheng Institute of Optics and Fine Mechanics. In the field of measurement instruments, East China Institute of Engineering has designed and produced Tammann inteferometers. This instrument was already used in China. Most of other measurement apparatus for various measurements such as scattering coefficient, absorption, ratio of optical attenuation, laser property, etc are non-standard apparatus developed by individual institutions themselves. Generally the conditions of characterization of laser crystals are still very poor; some fields are still blank (for example, quantum efficiency).

6. AN ESTIMATION OF THE FUTURE AND SOME SUGGESTIONS

For the past several decades the development of laser crystals was fast in China, and a quite strong basis and research force were already built up. As a general summary, in the field of laser crystal research and production, China is still behind the United States and Soviet Union with a big distance, but China is leading ahead of other nations in some aspects. It is anticipated that in the next 10-15 years, some of the common crystals can meet the needs of China and also can be exported. We will produce several new

laser crystals with good properties and good values for application. It is possible that some special equipment and whole packages of technology will be transfered to other countries.

In reviewing the progress of the past years, we should also see the weakness in this field.

In order to further develop the laser crystals of China, I make several suggestions as follows.

(1) Further carry out intensive studies of crystal defects. Combining crystal growth technology and crystal properties, attention should be paid to solve quality problems of the common crystals. In the next 5 years, the problems related to crystal growth of high quality large size crystals such as YAG, ruby, YLF, $Cr:BeAl_2O_4$, Nd:Cr:GSGG, CR:GSGG, should be solved. Production on an industrial scale should be organized in specific plants.

(2) Strengthen the basic research of some structural, and property studies. Investigate new type excitation ions and base materials. Exploit new mechanisms of transition and functional effects. The major research topics in the next 10 years might be as follows. (a) investigate tunable laser crystals using end-phonon and other transition systems. (b) Exploit new wavelengths using rare earth ions. Exploit high efficiency new wavelength laser crystals by applying sensitizers, anti-excitation, cascade, et cetera. (c)

investigate color center laser crystals. Improve the obtained color center crystals or develop new crystals, make intensive investigation of the physical and chemical processes of color centers. Solve the problem of heat stability; and make real applications as early as possible. (d) investigate multi-functional laser crystals. (e) Investigate new laser materials of condensed materials.

(3) Pay attention to the basic facility development related to crystal growth and related technology. There should be several national centers of crystal growth, optical processing, equipment research, characterization of instrument development. In order to change the backward situations, several sets of advanced equipment, instruments and whole items should be inported.

(4) Strengthen the training of scientific and technical personnel. It is suggested that crystal majors should be established in several universities. More graduated students withcrystal major should be enrolled. Send more students and visiting scholars of crystal majors abroad to receive advanced training. Encourage academic societies to organize in-position training programs.

(5) Further carry out the policy of adjustment. Solve the dispersive, repetitive, disorderly situations of research and production from the viewpoint of system organization.

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